

Thermodynamic process

- * The transformation of a system between two states describes a path, which is called a **thermodynamic process**.

- * There are infinite paths to connect two states

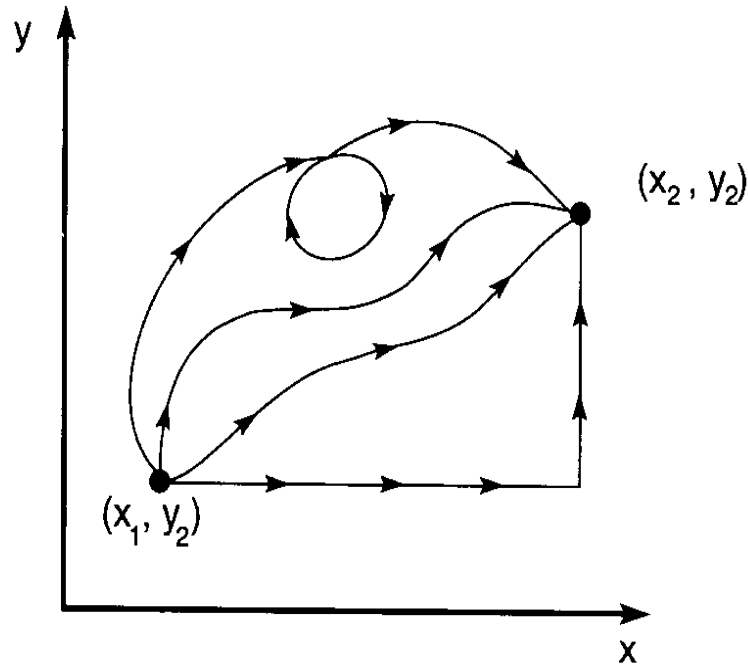


Figure 2.4 Possible thermodynamic processes between two states: (x_1, y_1) and (x_2, y_2) .

Thermodynamic process

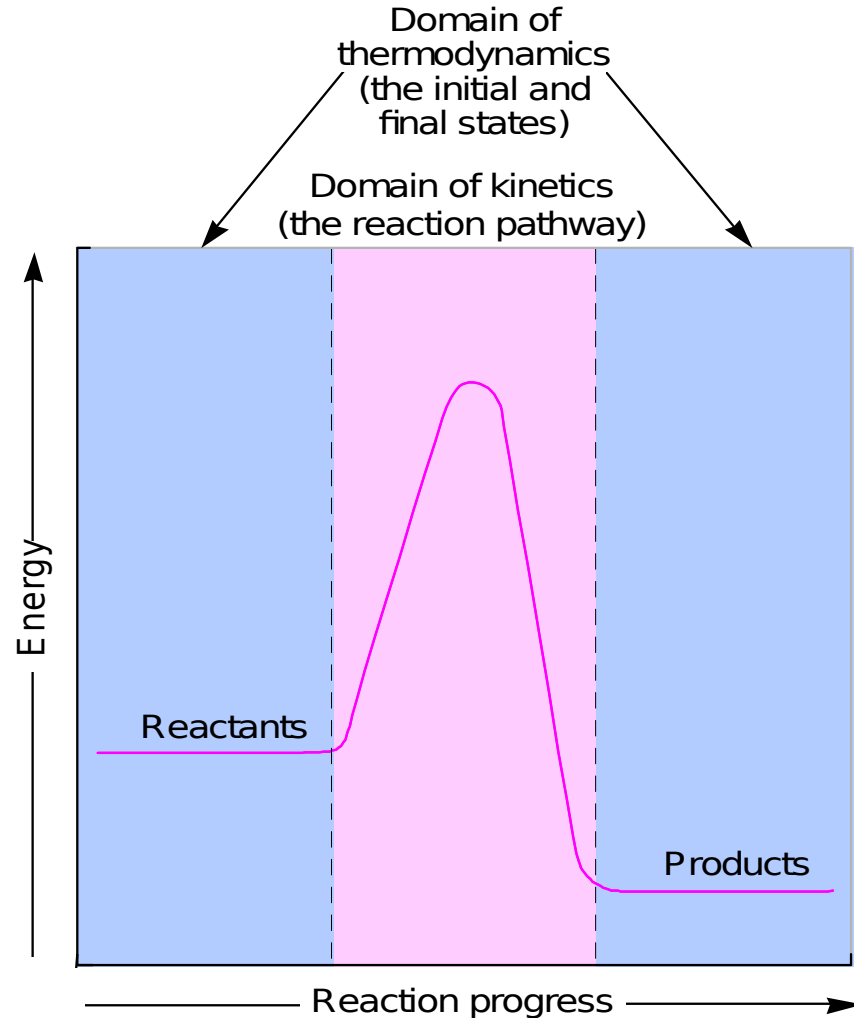
Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.

Kinetics & Thermodynamics

Chemical kinetics focuses on the pathway between reactants and products--the kinetics of a reaction depends on activation energy, temperature, concentration, and catalysts.

Thermodynamics only considers the initial and final states.

To describe a reaction fully, both kinetics and thermodynamics are necessary.



The rate of a reaction depends on the pathway from reactants to products. Thermodynamics tells whether the reaction is spontaneous and depends on initial & final states only.

Thermodynamic process

- From the point of view of the direction of the flow, spontaneous and non-spontaneous processes are distinguished.
- The processes that take place in the system by themselves, without interference from the environment, are called spontaneous, natural or positive.

Spontaneous Processes

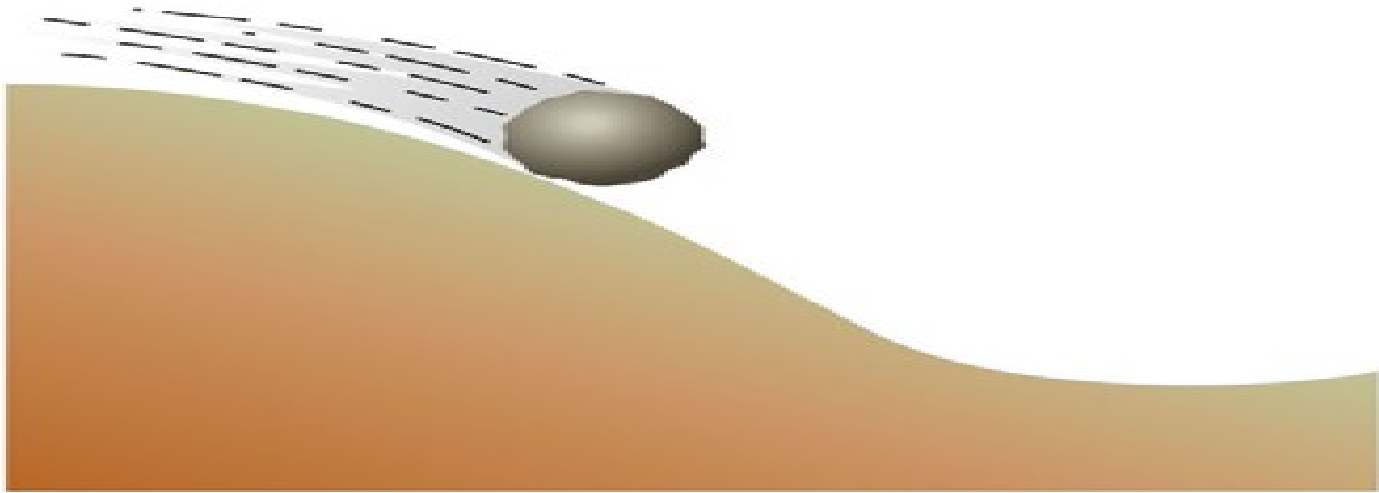
- A **spontaneous process** is a physical or chemical change that occurs by itself .
- Examples include:
- A rock at the top of a hill rolls down.
- Heat flows from a hot object to a cold one.
- An iron object rusts in moist air.
- These processes occur without requiring an
- outside force and **continue until**

What are some examples of spontaneous processes?

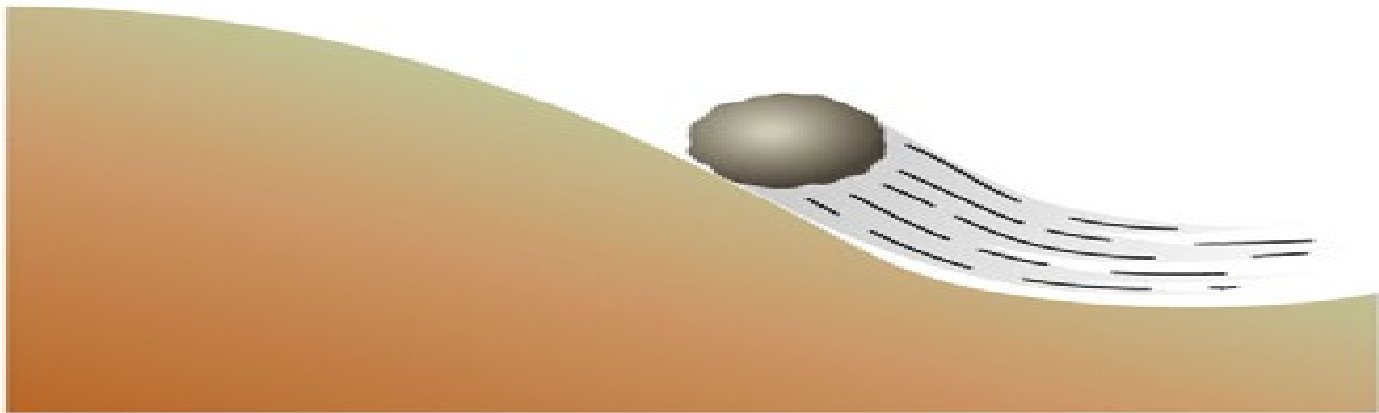
A process that *does occur* under a given set of conditions is considered spontaneous.

- For example, a waterfall flows downhill, but never up, spontaneously.
- Heat flows from a warmer object to a cooler one, but the reverse never happens spontaneously.
- Iron exposed to water and oxygen forms rust, but rust does not spontaneously change back into iron.

Spontaneous Processes

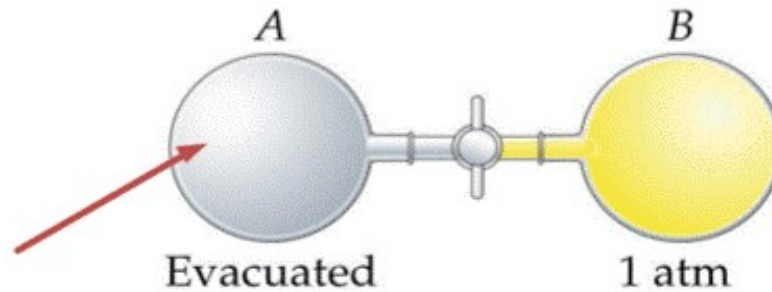


Spontaneous process



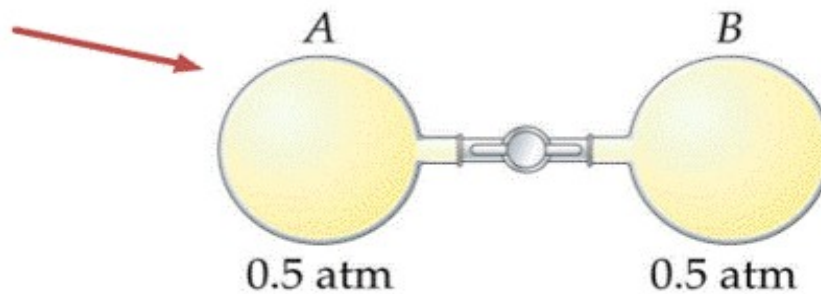
Nonspontaneous process

Spontaneous Processes



(a)

Spontaneous $\longleftrightarrow$ Not spontaneous



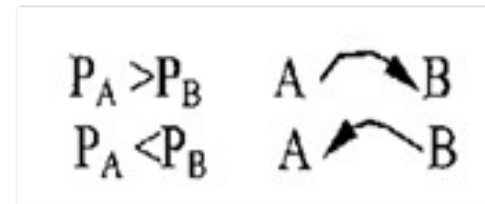
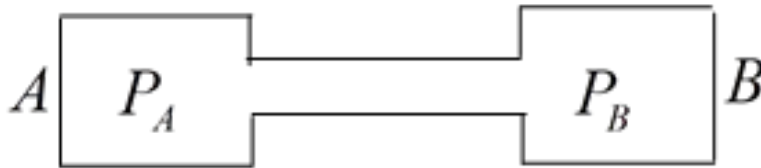
(b)

The second law of thermodynamics and its application to physicochemical processes

- The second law of thermodynamics answers the questions:
 - 1) Is the process possible?
 - 2) If so, in which direction will it go;
 - 3) Until when it will flow (i.e. its limit).

thermodynamics and its application to physicochemical processes

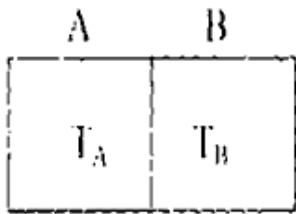
- Example 1. The gas expands and fills the free volume, but does not spontaneously compress to a smaller volume.



- Thus, for this process, there is a criterion (thermodynamic parameter) - the pressure that determines the direction of the spontaneous transition and its limit (that is, the state of equilibrium).

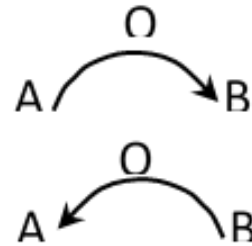
The second law of thermodynamics and its application to physicochemical processes

- Example 2. In the case of a heat transfer from a warmer body to a less heated one, the criterion is temperature.



$$T_A > T_B$$

$$T_A < T_B$$



- 1. For heat transfer to be possible, there must be $T_A \neq T_B$.
- 2. The process will go towards decreasing temperature.
- 3. The process will continue until the temperature is equalized, that is, when $T_A = T_B$.

The second law of thermodynamics

- Clausius formulation (1850):
- Heat alone cannot move from a colder to a warmer body, while heat transfer from a warm to a cold body may be the only result of processes

The second law of thermodynamics

- Thomson's formulation (1851):
- No set of processes can be reduced only to the conversion of heat into work, while the conversion of work into heat can be the only result of the process.

The second law of thermodynamics

- Ostwald's wording:
- It is impossible to create a perpetual motion machine of the second kind, i.e. such a machine that would work only by absorbing heat from the environment without transferring part of the heat to the refrigerator (it is impossible to turn all the internal energy of

The second law of thermodynamics

- Boltzmann formulation:
- An isolated system evolves primarily in the direction of greater thermodynamic probability.

The second law of thermodynamics

- Let's consider one more example. Suppose that for $T = \text{const}$ and $p = \text{const}$, we have the reaction:
 - $bB + dD \rightarrow gG + rR$
- Is there a process in this system? If so, in which direction? And to what extent? It is clear that the thermodynamic parameter "pressure" here does not help, "temperature" - too. All substances are at the same pressure and at the same temperature. For example, there are a lot of N_2 and O_2 in the audience, but why they do not interact by reaction:
 - $N_2 + O_2 \rightarrow 2NO$
- The process of stoichiometry is possible, by the number of molecules possible, but why is this process not going on? In the first two examples we have the parameters (P and T), by which we can determine whether the process is possible. One can conclude: apparently neither P nor T , and another thermodynamic parameter (associated with P and T) can determine this system. Such a criterion is a parameter (the thermodynamic function of the state of the system), which is called entropy.

The First Law of

Thermodynamics Does Not

Predict Spontaneous Change

Energy is conserved. It is neither created nor destroyed,

but is transferred in the form of heat and/or work.

$$\Delta E = q + w$$

The total energy of the universe is constant:

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}} \text{ or } \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = \Delta E_{\text{univ}} = 0$$

*The law of conservation of energy applies to **all** changes, and does **not** allow us to predict the **direction** of a spontaneous change.*

ΔH Does Not Predict Spontaneous Change

*A spontaneous change may be exothermic or endothermic. Spontaneous **exothermic** processes include:*

- freezing and condensation at low temperatures,*
- combustion reactions,*
- oxidation of iron and other metals.*

*Spontaneous **endothermic** processes include:*

- melting and vaporization at higher temperatures,*
- dissolving of most soluble salts.*

The sign of ΔH does not by itself predict the direction of a spontaneous change.

Spontaneous Change

A **spontaneous** change is one that occurs **without** a continuous input of energy from outside the system.

All chemical processes require energy (**activation energy**) to take place, but once a spontaneous process has begun, no further input of energy is needed.

A **nonspontaneous** change occurs only if the surroundings **continuously** supply energy to the system.

If a change is spontaneous in one direction, it will be nonspontaneous in the reverse direction.

Microstates and Dispersal of

Energy

- *Just as the electronic energy levels within an atom are **quantized**, a system of particles also has different allowed energy states.*
- *Each quantized energy state for a system of particles is called a **microstate**.*
 - *At any instant, the total energy of the system is dispersed throughout one microstate.*
- *At a given set of conditions, each microstate has the **same** total energy as any other.*
 - *Each microstate is therefore equally likely.*
- *The larger the number of possible microstates, the larger the number of ways in which a system can disperse its energy.*

Entropy

y

*The number of microstates (W) in a system is related to the **entropy** (S) of the system.*

$$S = k \ln W$$

*A system with **fewer** microstates has **lower entropy**.*

*A system with **more** microstates has **higher entropy**.*

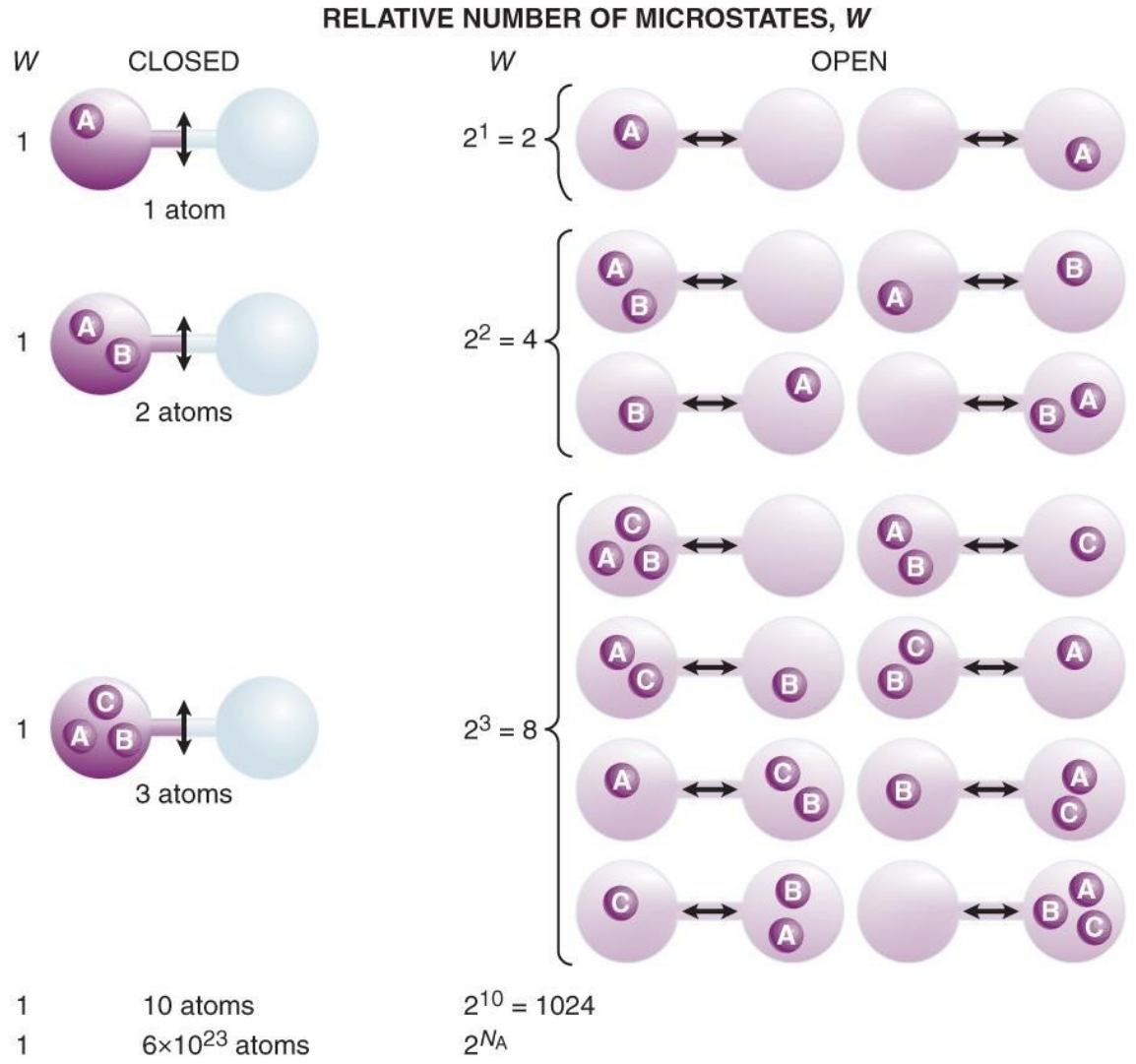
All spontaneous endothermic processes exhibit an increase in entropy.

*Entropy, like enthalpy, is a **state function** and is therefore independent of the path taken between*

Expansion of a gas and the increase in number of microstates.

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When the stopcock opens, the number of microstates is 2^n , where n is the number of particles.



The concept of entropy

- For the adiabatic process ($Q = 0$), equation of first law of thermodynamic has the form:
- $A = -\Delta U$
- Hence it can be assumed that the entire internal energy of the system can be spent on work. That is, it would be possible to use inexhaustible energy resources, for example, rivers, seas, oceans. However, not all internal energy turns into work, part of it remains connected, i.e. devalued
 - $U = F + g$
- where F is the free energy or Helmholtz energy or isochoric-isothermal potential. This is that part of the internal energy that can be converted into work (at constant T and V); g -devaluated energy that can not be turned into work;

The concept of entropy

$$\bullet g = T \cdot S$$

- where S is a measure of impaired or bound energy, reduced heat or entropy.
- Entropy is a measure of bound energy, useless energy, that is, it is that part of the internal energy that can not be turned into work.

$$\bullet \text{Then } U = F + TS$$

- Entropy is a function of the state of the system. Its change in any process depends only on the initial and final states, but does not depend on the path of the process:

$$\bullet \Delta S = S_2 - S_1$$

- In an isolated system, spontaneous processes occur in the direction of increasing entropy. That is, if as a result of calculation, it turns out that the entropy increases, then the process or reaction is possible (isolated is the

The concept of entropy

- Entropy size: [J / molK] or entropic units / mole.
- that is, the change in entropy is equal to the heat divided by the absolute temperature.
$$\Delta S = \frac{Q}{T}$$
- For an reversible transition of an infinitely small quantity, the heat is δQ :
$$dS = \frac{\delta Q}{T}$$
-
- S- is a function of the state; therefore, the total differential (dS), and Q-is not a function of the state, therefore δQ :
- $\delta Q_{\text{form}} = TdS$

The concept of entropy

- Irreversible are the processes after which the system can no longer be returned to the initial state without any changes in it or in the environment itself. For example, the process of transfer of heat from a warmer body to a less heated body is an irreversible process and it can not be carried out in the opposite direction without having to work on it.

- For an irreversible process

$$dS \geq \frac{\delta Q}{T}$$

In general

The concept of entropy

- Thus, in isolated systems, spontaneously only those processes would be goes that are accompanied by an increase of entropy

$$\bullet dS \geq 0$$

- the limit of the flow of a spontaneous process in isolated systems is to achieve the maximum value of entropy for these conditions. Thus, in isolated systems, S is a criterion for the direction of the process and an

The combined equation of the first and second laws of thermodynamics

- The mathematical expression of the first law of thermodynamics has the form:
- $\delta Q = du + \delta A$
- Expression of the second law:
- $\delta Q \leq TdS$
- If in the system only the work of expansion is performed, then:
- $\delta A = pdv$
- We substitute the values of δQ and δA from equations into equation :
- $TdS \geq du + pdv$
- This is the combined equation of two laws. It follows from this that entropy is a function of internal energy and volume: $S = f(u, v)$.

Introduction

The word “entropy” was created by German physicist “Rudolf Clausius” in 1854.

The word has a Greek origin, its first part reminds us of “energy” and the second part is from “tropos” which means turning point.

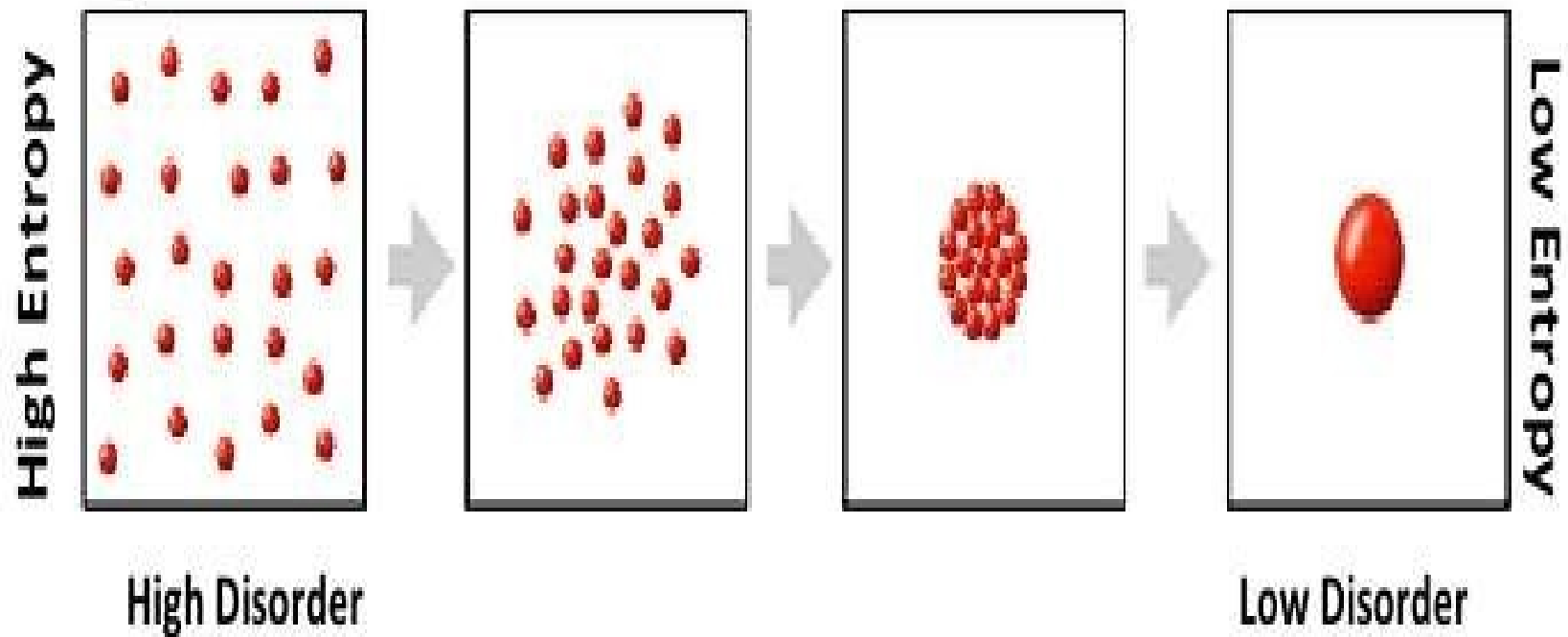


Rudolf Clausius (1822 - 1888)

CONCEPT

The idea of entropy comes from a principle of thermodynamic dealing with energy .It usually refers to idea that everything in the universe eventually moves from order to disorder , and entropy is the measurement of that change.

- Physicists use entropy to measure the amount of disorder in a physical system.
- In information theory , entropy is the expected value (average) of the information contained in each message received.
- It can be considered as the degree of randomness in a message



*Thus we can say that
more disorder = more
entropy more order =
less entropy*

law of Entropy

*The second **law** of thermodynamics, “**entropy** of an isolated system always increases.”*

Or in other words

“The entropy can be created but not destroyed”

Unit of Entropy

The SI unit for Entropy (S) is

Joules per Kelvin (J/K).

Clausius is also gives the relation between the units i.e.

***1 Clausius (Cl) = 1 (cal/°C) =
4.1868 (J/K)***

CLASSIFICATION

- ✓ *Thermodynamical entropy*
- ✓ *Statistical entropy*
- ✓ *Entropy in classical world*
- ✓ *Entropy in quantum world*

Thermodynamical Entropy

Entropy is defined using Clausius inequality

$$\oint \left(\frac{\delta Q}{T} \right) \leq 0$$

The cyclic integral of $\frac{\delta Q}{T}$ can be viewed as the sum of all these differential amounts of heat transfer divided by the temperature at the boundary.

$$\oint \left(\frac{\delta Q}{T} \right) = 0 \quad (\text{for reversible cycle})$$

$$\oint \left(\frac{\delta Q}{T} \right) < 0 \quad (\text{for irreversible cycle})$$

by definition:

Let's define a thermodynamic property entropy (S), such that

$$\oint \left(\frac{dQ}{T} \right) > 0 \quad (\text{for impossible cycle})$$

Standard Molar Entropies

S° is the **standard molar entropy** of a substance, measured for a substance in its **standard state** in units of J/mol·K.

The conventions for defining a standard state include:

- 1 bar for gases
- 1 mol/L for solutions, and
- the pure substance in its most stable form for solids and liquids.

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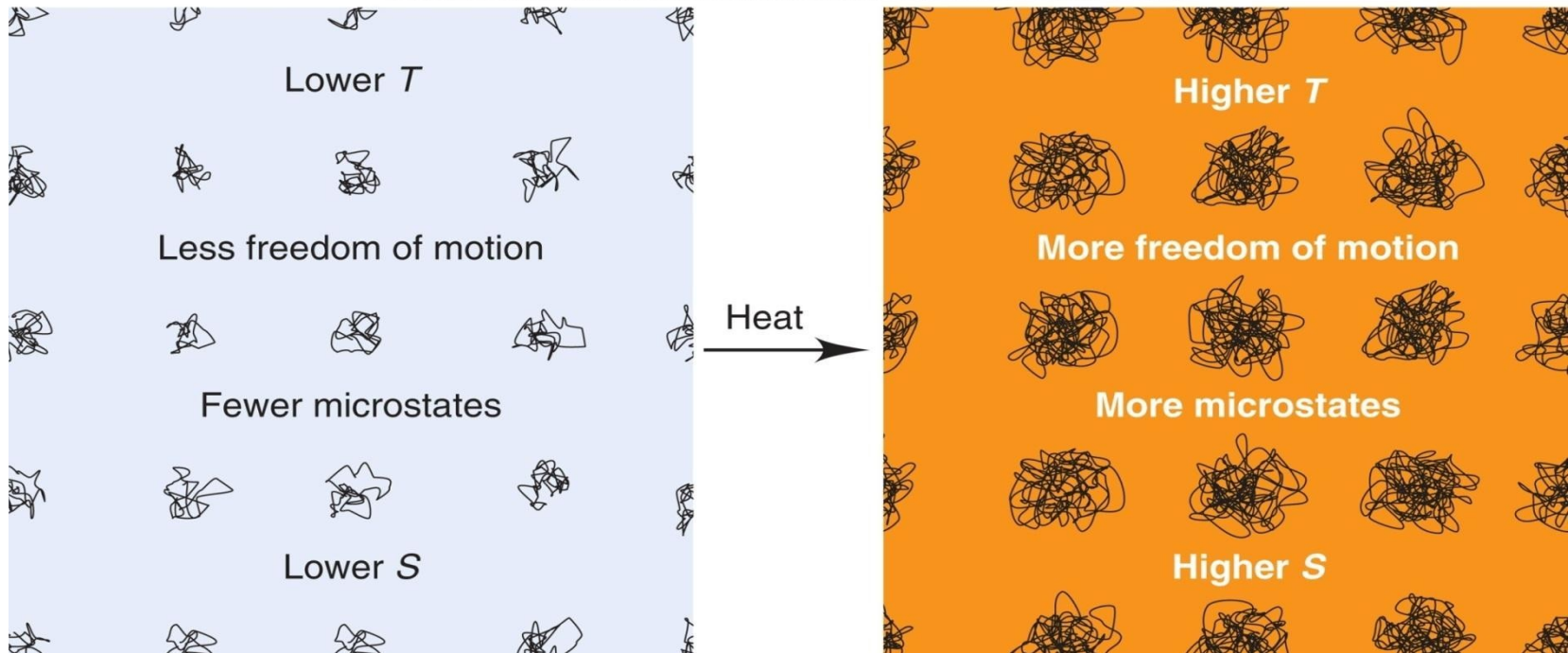
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Factors Affecting Entropy

- *Entropy depends on temperature.*
 - *For any substance, S° increases as temperature increases.*
 - *Entropy depends on the physical state of a substance.*
 - *S° increases as the phase changes from solid to liquid to gas.*
- *The formation of a solution affects entropy.*
- *Entropy is related to atomic size and molecular complexity.*
 - *Remember to compare substances in the same physical state.*

Effect of temperature on entropy

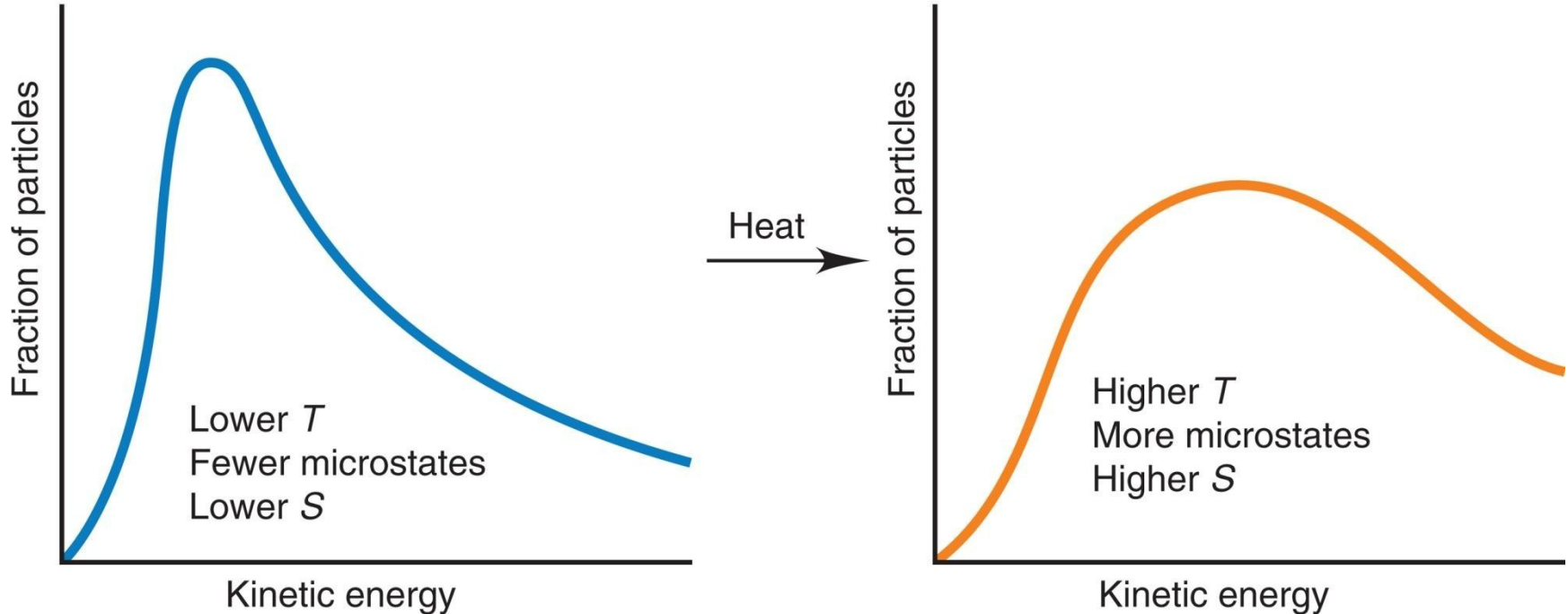
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Computer simulations show each particle in a crystal moving about its lattice position. Adding heat increases T and the total energy, so the particles have greater freedom of motion, and their energy is more dispersed. S therefore increases.

Effect of temperature on entropy

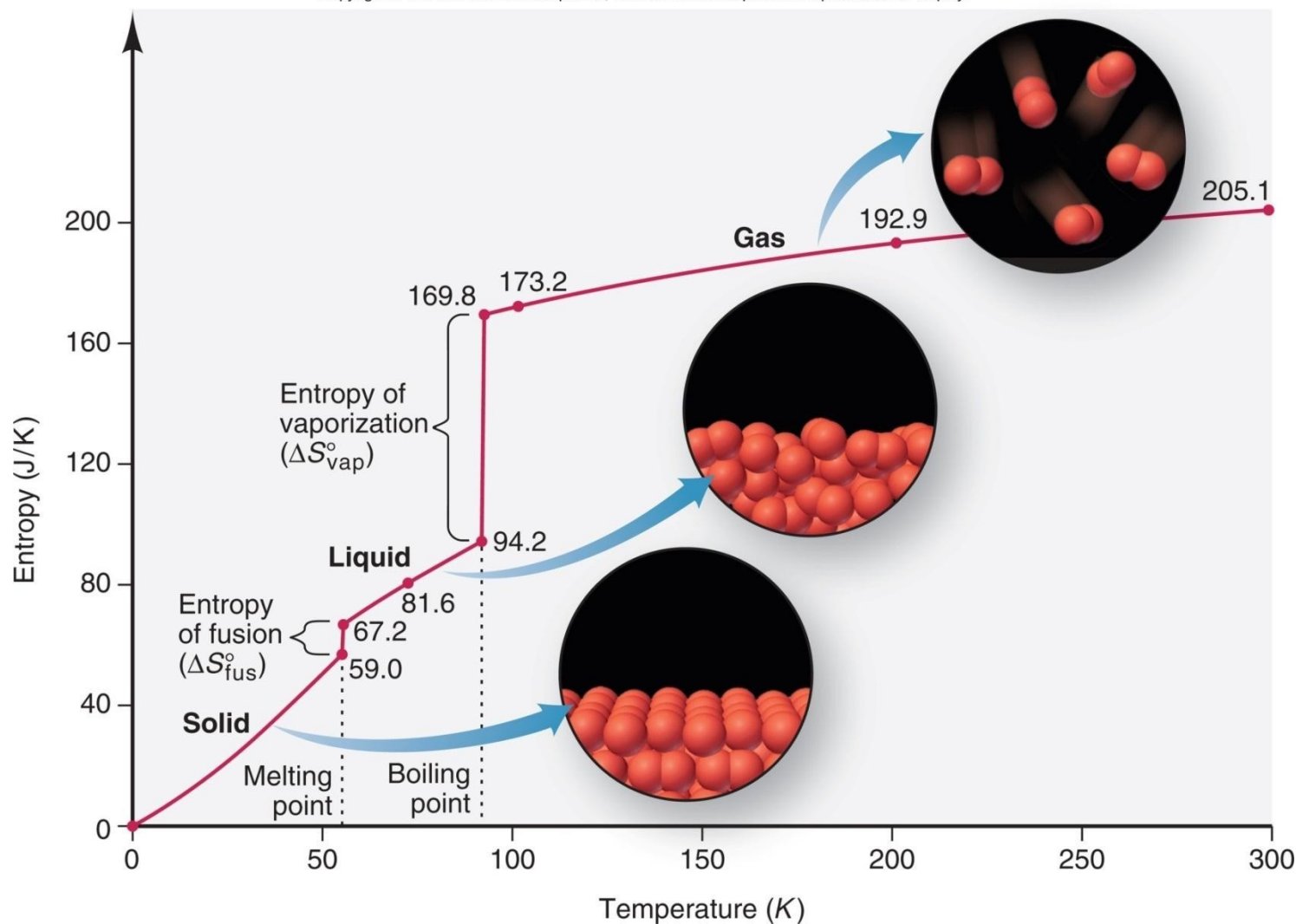
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At any T , there is a range of occupied energy levels and therefore a certain number of microstates. Adding heat increases the total energy (area under the curve), so the range of occupied energy levels becomes greater, as does the number of microstates.

The increase in entropy during phase changes

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Entropy and Atomic Size

*S° is **higher** for **larger** atoms or molecules of the same type*

	Li	Na	K	Rb	Cs
Atomic radius (pm)	152	186	227	248	265
Molar mass (g/mol)	6.941	22.99	39.10	85.47	132.9
$S^\circ(s)$	29.1	51.4	64.7	69.5	85.2

	HF	HCl	HBr	HI
Molar mass (g/mol)	20.01	36.46	80.91	127.9
$S^\circ(s)$	173.7	186.8	198.6	206.3

Entropy and Structure

For allotropes, S° is higher in the form that allows the atoms more freedom of motion.

S° of graphite is $5.69 \text{ J/mol}\cdot\text{K}$, whereas S° of diamond is $2.44 \text{ J/mol}\cdot\text{K}$.

For compounds, S° increases with chemical complexity.

	NaCl	AlCl₃	P₄O₁₀	NO	NO₂	N₂O₄
$S^\circ(\text{s})$	72.1	167	229			
$S^\circ(\text{g})$				211	240	304

*These trends only hold for substances in the **same physical state**.*

Entropy Changes in the System

The **standard entropy of reaction**, ΔS°_{rxn} , is the entropy change that occurs when all reactants and products are in their standard states.

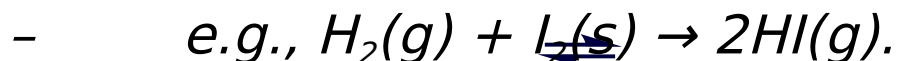
$$\Delta S^\circ_{rxn} = \Sigma m S^\circ_{products} - \Sigma n S^\circ_{reactants}$$

where m and n are the amounts (mol) of products and reactants, given by the coefficients in the balanced equation.

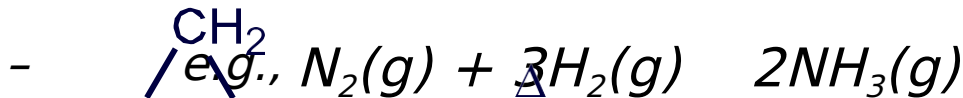
Predicting the Sign of $\Delta S^\circ_{\text{rxn}}$

We can often predict the **sign** of $\Delta S^\circ_{\text{rxn}}$ for processes that involve a **change** in the **number of moles of gas**.

- $\Delta S^\circ_{\text{rxn}}$ is **positive** if the amount of gas increases;



- $\Delta S^\circ_{\text{rxn}}$ is **negative** if the amount of gas decreases;



- ΔS° is likely to be **positive** if a new structure forms that has more freedom of motion.

